Feasibility Study for the USAF, relating to provision of samples of new perfluoropolyethers, for testing as novel lubricants

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Provision of Samples of New Perfluoropolyethers as Potentially Novel Lubricants - Feasibility Study

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Perfluorinated polyethers are an important component of the long-term strategy of the USAF., as high-temperature lubricants. Current, commercially-available materials are exemplified by the 'KRYTOX' (1) (DuPont), 'FOMBLIN' (2) (Montefluos), and 'DEMNUM' (3) (Daikin) fluids. All of these products involve a polymerisation, of a fluorinated precursor, which can be difficult to control. In particular, it is difficult to obtain high molecular weight material.

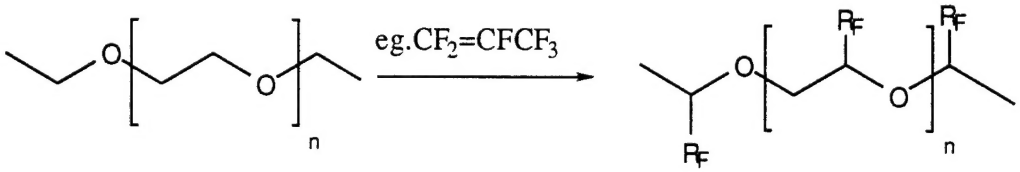
$[-OCF_2CF(CF_3)-]_n$ (1)

$[-OCF_2CF_2-]_n$ (2)

$[-OCF_2CF_2CF_2-]_n$ (3)

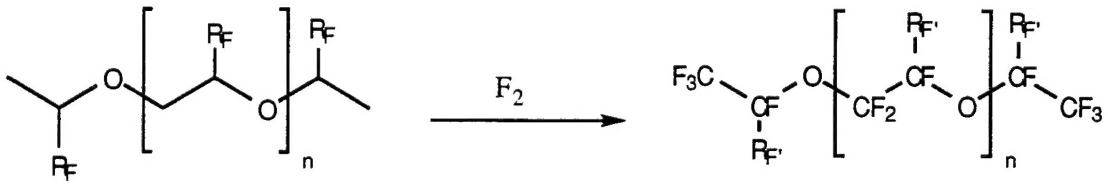
In an earlier grant from the USAF (AFOSR-87-0324) we devised an alternative approach in which two steps are involved:

A A polyether of known molecular-weight spread eg.(4) is modified, in a free radical process, with a fluorinated alkene.



(4) (5) e g $R_F = CF_2CFHCF_3$

B The extensively modified ether (5) is then fluorinated to a perfluoro-polyether (6).



(5) e g $R_F = CF_2CFHCF_3$ (6) e g $R_F = CF_2CF_2CF_3$

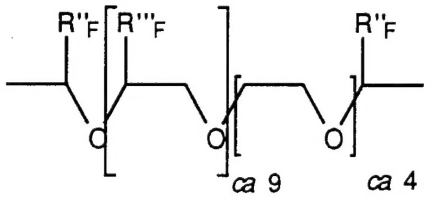
Thus we have, in theory, (i) a pre-determined molecular weight range, (ii) the potential to vary the polyether, (iii) the potential for a wide range of structural types by varying the nature of perfluoro-alkene, and (iv) the potential for varying the side chain content. Clearly, considerable 'tailoring' of the products is possible if this methodology is developed.

We have a patent position [R.D. Chambers, US Pat. 4877905 (31st October, 1989).] on the method described above. The contract involves scale-up for the purposes of lubricant testing.

Work completed in the first part

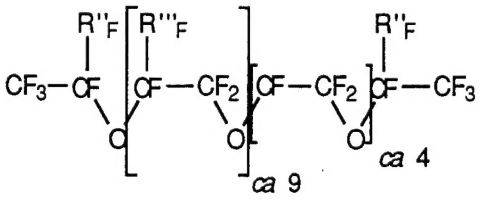
In a contract between 1 July and 31 December 1992, we developed the synthesis of the modified polyether (5a) and can now carry out the reaction smoothly on a one kilo scale. We have subsequently fluorinated this material, using elemental fluorine, giving (6a).

$R''_F = CF_3CFHCF_2$ (predom) or H
$R'''_F = CF_3CFHCF_2$



[5a]

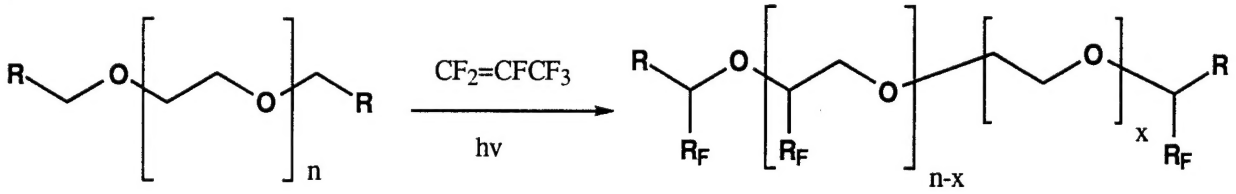
$R''_F = CF_3CF_2CF_2$ (predom) or F
$R'''_F = CF_3CF_2CF_2$



[6a]

Feasibility Study

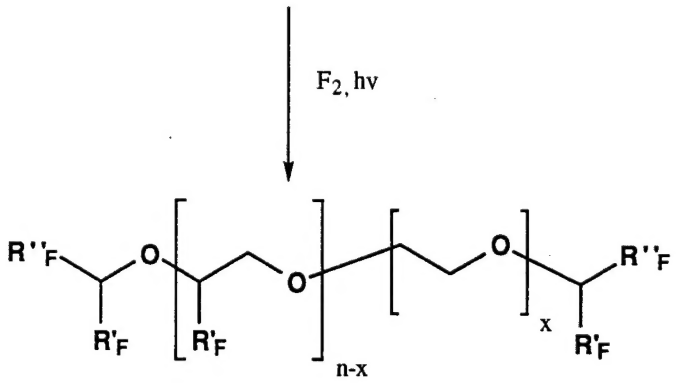
We have now worked for 10 weeks, in a 6-month period for the contract, which aims to provide at least one 10-20g sample of the novel perfluorinated polyether (**9**), where n-x will have an average value of ca. 13 or greater.



(**7**) e g n = ca. 22

(**8**) n-x = ca 13

(R = H or alkyl, $R_F = CF_2CFHCF_3$)



(**9**)

($R'_F = CF_2CF_2CF_3$, R''F = CF_3 or F, all unmarked bonds to F

The starting material (7) is of higher molecular weight than the sample provided earlier. We have now demonstrated that modification of (7) to give (8), (where n-x=13) occurs readily on a suitable scale (150 g). This process is capable of being further scaled up if required. Furthermore, we have demonstrated that fluorination of (7) can be achieved by the partial fluorination of a trial sample. It is this initial stage of fluorination which has in the past proved difficult to control.

Therefore, very significant progress towards the aim of the contract has already been made and the results completely verify the feasibility of our proposals.